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## COMPLETE SPECIFICATION

## Improvements in or relating to Emulsion Polymerisation

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America).

I, CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention pertains to the polymerization of unsaturated materials in aqueous emulsion.

Synthetic rubber-like materials have been prepared by polymerizing one or more conjugated diolefins or by interpolymerizing one or more conjugated diolefins with copolymerizable materials containing a single olefinic double bond such as styrene, substituted styrenes, acrylonitrile, methacrylonitrile, acrylic acid esters, unsaturated ketones and the like in aqueous emulsion, using a compound capable of liberating oxygen under the reaction conditions such as hydrogen peroxide, benzoyl peroxide and alkali metal or ammonium persulfates and perborates as catalysts.

As ordinarily carried out, the reactants are emulsified in from an equal to a two-fold quantity of water using as the emulsifier water-soluble soaps such as the alkali metal or ammonium oleates and stearates as well as various surface active agents such as salts of alkylated naphthalene sulfonic acids, salts of aliphatic and olefinic sulfonic acids, salts of fatty alcohol sulfuric acid esters and also acid addition salts of high molecular weight alkyl amines. A polymerization catalyst such as potassium persulfate and preferably a suitable polymerization modifier is added and the mixture maintained under agitation at temperatures of from 20—60°C.

for a period sufficient to cause at least about 70% of the monomer materials to become converted to a high molecular weight polymer. The polymers formed vary from hard, resinous materials to soft, rubber-like materials depending upon the particular monomers and the proportions in which they are used and the reaction conditions applied. In general, soft rubbery polymers result when the diolefin is the preponderant material, provided, of course, that other reaction conditions are right.

In the polymerization or copolymerization of conjugated diolefin hydrocarbons in aqueous emulsion the reaction times have been found to be rather long to reach approximately 70—75% conversion of the monomer materials used when using reaction temperatures in the range of 25—40°C. Attempts have been made to speed up the rate of reaction as by raising the temperature at which the reaction is conducted, but this, in general, has resulted in inferior polymerizates. Certain materials which have a modifying effect upon the polymerization to give more plastic polymers also have a promoting effect. Such materials include primary, secondary and tertiary alkyl and aralkyl mercaptans used preferably in the presence of a peroxide or per-salt. (Certain promoters such as carbon bisulfide, aldehydes, oxides and salts of polyvalent metals have been proposed but use of such materials has not made possible the desired rates of reaction in the temperature range of 20—40°C.) The most generally used polymerization modifiers are the aliphatic mercaptans containing more than six and preferably about twelve carbon atoms per molecule. Although these mercaptans promote or increase the speed of reaction as well as cause the formation of more plastic polymers, there is still a demand for other and improved types of promoting agents.

It is the main object of this invention

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to activate the emulsion polymerization of conjugated diolefins or of mixtures of conjugated diolefins or mixtures of conjugated diolefins with certain copolymerizable compounds without detrimentally affecting the polymer product quality.

The polymerization of olefinic materials in aqueous emulsion, in the presence of an oxygen-yielding catalyst is, thus, well known. When the monomers are diolefins or mixtures of diolefins or mixtures of diolefins with monoolefinic monomers of the types described later, the products are generally of a rubbery nature. Polymers of monoolefinic materials such as acrylates, methacrylates and acrylonitrile, are more in the nature of resinous bodies.

It has also been proposed in the past to prepare polymers and copolymers by emulsion polymerization as just described and in the presence of a substantial amount of a mutual solvent for the monomer or monomers and the water, examples of such solvents being amines and alkanolamines.

It has now been found that in an emulsion polymerization of the type referred to, excepting of course those in which substantial amounts of amines are present, the presence of a  $C_2-C_6$  amine having only one nitrogen atom per molecule in an amount not substantially greater than 0.5% by weight based on the reactants, has a marked promoting effect on the polymerization reaction.

The present invention accordingly comprises a process for the polymerization of olefinic materials in aqueous emulsion of the type referred to, wherein there is present in the reaction mixture an amount not substantially in excess of 0.5% by weight based on the reactants of a  $C_2-C_6$  amine having only one nitrogen atom per molecule.

The preferred amines may conveniently be classified by reference to their ionization constants which fall between those of morpholine ( $2.44 \times 10^{-6}$ ) and piperidine ( $1.6 \times 10^{-3}$ ), e.g. monoethylamine, diethylamine, diethyl amino ethanol. Some of the suitable amines do however fall outside this classification, e.g. diethanolamine ( $7.62 \times 10^{-7}$ ).

There may also be employed derivatives of such amines, such as hydroxy amines wherein the  $-CH$  group is attached to a carbon atom, amino ethers, amine salts such as hydrochlorides or sulfates or chloroamines. The preferred monomers to be polymerized are those which yield synthetic rubbery materials, namely diolefins and mixtures of diolefins with monoolefinic compounds.

Thus, this invention is applicable to the production of emulsion polymers of conjugated diolefins such as butadiene, isoprene, piperylene, dimethyl butadiene chloroprene, methyl pentadiene, cyanoprene, phenyl butadiene and the like taken singly or in combination, to the production of copolymers of one or more of such diolefins with a compound containing a single double bond such as acrylonitrile, methacrylonitrile, acrylic acid esters such as methyl acrylate and methyl methacrylate, fumaric acid esters such as ethyl fumarate or other alkyl fumarate and unsaturated ketones such as methyl vinyl ketone or methyl isopropenyl ketone and the like or to the polymerization of one or more monoolefinic compounds such as the foregoing nitriles, ketones and esters.

The polymerization is ordinarily effected by dispersing one part of the monomer or monomer mixture in from about one to two parts of water containing a suitable emulsifying agent and a polymerization catalyst. A suitable polymerization modifier or promoter may also be provided in the reaction mixture if desired.

The emulsifiers employed are the alkali metal or ammonium salts of higher molecular weight fatty acids such as oleic acid, stearic acid, palmitic acid, as well as mixtures of fatty acids such as are obtained by the selective hydrogenation of tallow acids and also surface active compounds such as the alkali metal salts of sulfonic acids or fatty alcohol sulfates, for example, sodium salts of isobutylnaphthalene sulfonic acid or tetraisobutenyl sulfonic acid, sodium dodecyl sulfate and also acid addition salts of high molecular weight alkyl amines such as dodecyl amine hydrochloride or acetate. The amount of emulsifier used is ordinarily between 0.5 to 5 weight per cent based upon the monomers used.

The catalysts which are used are substances which are capable of liberating oxygen under the conditions employed in the polymerization and include such compounds as hydrogen peroxide, benzoyl peroxide, hydrogen peroxide addition compounds, hydrogen peroxide with metal activators, tertiary butyl hydroperoxide, perborates, persulfates and organo metallic compounds such as iron carbonyl. The amount of catalyst used is ordinarily 0.05 to 0.6 weight per cent based upon the monomers present.

The  $C_2-C_6$  amino compounds which may be used as polymerization promoters in accordance with the present invention are water-soluble primary, secondary and

tertiary amines and water-soluble derivatives thereof and generally have an ionization constant of at least  $2.44 \times 10^{-6}$ . The most active of these compounds are the aliphatic, alicyclic or heterocyclic amines, such as monoethyl amine, diethyl amine, diethyl amino ethanol, piperidine and morpholine. Other amines and derivatives which may be used in accordance with this invention are propyl, butyl, amyl, hexyl, dipropyl, trimethyl, dimethyl-ethyl and triethyl amines and tetraethyl ammonium hydroxide, pyrrolidine, piperazine, a mono-, di- and tri-ethanolamine and the methyl or ethyl ethers of dimethyl- or diethylamino ethanol, chloromethyl amine or chlorobutyl amine. The amine promoters are preferably used in amounts of 0.05 to 0.5% by weight based upon the reactants.

The amine type promoters are advantageously used in combination with polymerization modifiers, particularly aliphatic mercaptans containing at least six carbon atoms such as heptyl, octyl, diisobutyl, dodecyl or "Lorol" (Registered Trade Mark) mercaptan or xanthogen polysulfides such as diisopropyl xanthogen disulfide. In lieu of the mercaptan, there may also be used certain mercaptan-vinyl compound addition products such as are obtained by reacting primary, secondary or tertiary mercaptans of varying molecular weight at room temperature in the presence of oxygen, with vinyl compounds such as acrylonitrile, methacrylonitrile, vinyl ethers or vinyl ketones.

The following examples, in which all parts and percentages are by weight unless otherwise specified, are illustrative of the present invention but it is to be understood that this invention is not limited thereto:—

#### EXAMPLE 1

Several emulsion polymerization experiments were made in which butadiene and acrylonitrile were copolymerized in emulsion using a persulfate-mercaptan combination in conjunction with morpholine as a promoter in accordance with the present invention. The following recipe was used:—

Water	-	-	-	200	parts
Soap	-	-	-	4	"
"Lorol" Mercaptan	-	-	0.5		"
Potassium Persulfate	-	-	0.3		"

TABLE II.

% Morpholine	Temperature °C.	Time Hours	% Conv.	Mooney Viscosity 1 min. 4 mins.
0.1	24	13½	75	134 132
0.4	24	10	75	153 163

Acrylonitrile	-	-	-	26	parts
Butadiene	-	-	-	74	"
Morpholine	-	-	-	variable	80
Reaction Temperature	-	-	-	77°F.	
Reaction Time	-	-	-	14½ hrs.	

The results obtained are summarized in Table I below from which it may be seen that morpholine in a concentration as low as 0.05% based upon the reactants has a very definite promoting effect upon the reaction. Although a concentration of 0.8% of morpholine is about equally effective as 0.1% as far as promoting the reaction is concerned, it will be shown in Example 2 below that the use of larger amounts of amine is detrimental from the standpoint of product quality.

TABLE I.

PER CENT CONVERSION VS. MORPHOLINE CONCENTRATION IN THE SYNTHESIS OF ACRYLONITRILE-BUTADIENE COPOLYMERS			
% Morpholine (Based on Reactants)	% Conversion		
0	50		80
0.05	84		
0.1	91		
0.2	94		
0.4	95		85
0.8	93		

Similar results were obtained (i.e. 90% conversion) after 16½ hours at 25°C. when 0.2% of morpholine was used as a promoter and sodium lauryl sulfate was used as the emulsifier instead of the soap.

#### EXAMPLE 2.

Two runs were carried out in a 3 gallon stainless steel reaction vessel equipped with internal agitation. Each reaction charge was as given in Example 1, using a total charge of 3 Kg. of monomers. One run was made using 0.4% of morpholine, while in the other run only 0.1% was used. The results are summarized in Table II below from which it may be seen that the run with the larger amount of morpholine resulted in a less plastic product. Thus, although the concentration of the amine promoter is not critical from the standpoint of reaction rate, the concentration must be kept to a minimum in order to get products of good plasticity. By using larger concentrations of mercaptan modifier with the amine, it is possible to prepare polymers having Mooney Viscosities as low as 50 or less.

## EXAMPLE 3.

A number of experiments similar to those carried out in Example 1 were made substituting methyl isopropenyl ketone for the acrylonitrile and piperidine for morpholine. The data from these experiments are summarized in Table III below.

It may readily be seen therefrom that the piperidine to the reaction mixture brought about increases in conversion from about 10% to about 90% when mercaptan modifiers were present and from about 40% to 60% when isopropyl xanthogen disulfide was present.

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TABLE III.

COPOLYMERIZATION OF BUTADIENE AND METHYL ISOPROPENYL KETONE USING PIPER-

IDINE AS PROMOTER

Experiment No.	1	2	3	4	5	6	7
Water, cc.	400	400	400	400	400	400	400
Soap Flakes, Gms.	10	10	10	10	10	10	10
Methyl Isopropenyl Ketone, Gms.	50	50	50	50	50	50	50
"Lorol" Mercaptan, Gms.	0.9	1.1	1.5	0.9	1.1	—	—
Isopropyl Xanthogen Disulfide, Gms.	—	—	—	—	—	1.0	1.0
Potassium Persulfate, Gms.	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Butadiene-1, 3, Gms.	150	150	150	150	150	150	150
Piperidine, cc.	—	—	0.5	0.5	0.5	—	0.5
Reaction Time, Hrs.	18½	18½	18½	18½	18½	22½	22½
Reaction Temp., °C.	40	40	40	40	40	40	40
Product, Gms.	24	24	32	177	178	79.5	120
Conversion, %	12	12	16	88.5	89	39.7	60
Plasticity of Polymer	A	A	A	A	A	B	B

A=Not plastic.

B=Quite plastic.

Similar experiments were conducted to determine the effectiveness of piperidine on the polymerization of butadiene, the data from which is contained in Table IV.

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TABLE IV.

PIPERIDINE AS PROMOTER IN THE  
PREPARATION OF POLYBUTADIENE  
IN EMULSION

Water, cc.	400	400
Soap Flakes, Gms.	10	10
Tertiary Dodecyl Mercaptan, cc.	1.3	1.3
Potassium Persulfate, Gms.	0.5	0.5
Butadiene-1, 3, Gms.	200	200
Piperidine, cc.	1.0	—
Reaction Time, Hrs.	12	12
Reaction Temperature, °C.	60	60
Product, Gms.	180	166
Conversion, %	90	83

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## EXAMPLE 5

A series of runs were made preparing emulsion co-polymerizers of butadiene and acrylonitrile using varying amounts of piperidine. The following recipe was used:—

Water	200 parts
Soap	4 "
"Lorol" Mercaptan	0.5 "
Potassium Persulfate	0.3 "
Acrylonitrile	26 "
Butadiene	74 "
Piperidine	variable
Reaction Temperature	84°F.
Reaction Time, Hrs.	14.75

The results of these runs are summarized in Table V below from which it may be seen that about 0.3% of piperidine is optimum for this reaction system.

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TABLE V.

PER CENT CONVERSION VS. PIPERIDINE  
CONCENTRATION IN THE SYNTHESIS OF  
ACRYLONITRILE-BUTADIENE  
COPOLYMERS

Piperidine, Per Cent on Reactants	Conversion, Per Cent
0.	62.3
0.05	72.5
0.10	77.5
0.20	83.9
0.30	86.7
0.40	88.9
0.50	87.2
0.60	87.7
1.00	88.2

## EXAMPLE 6.

Three experiments were carried out simultaneously using the recipe as given in Example 1, except that methyl acrylate was used instead of acrylonitrile. The ratio of methyl acrylate to butadiene in the charge was 25/75. After 16 hours at 31°C., the following conversions were obtained.

% Morpholine Used	% Conversion
0.0	22.5
0.4	57.5
0.8	60.0

## EXAMPLE 7.

Two pressure bottle runs were made at a 105 temperature of 25–26°C., for 15 hours

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using the following recipes in order to demonstrate the efficacy of amine promoters in polymerization systems operated at a pH below 7.

	Run A	Run B
	parts	parts
Water - - - - -	400	400
Butadiene - - - -	148	148
Acrylonitrile - - -	52	52
10 Dodecylamine Hydrochloride - - - -	10	10
Potassium Persulfate -	0.6	0.6
Dodecyl Mercaptan - -	1.0	1.0
Morpholine - - - -	0.0	0.2

15 A conversion of 34% was obtained in Run A while Run B, carried out at the same temperature and for the same time as Run A, gave a conversion of 64%.

#### EXAMPLE 8.

20 A run was made in accordance with the recipe given in Example 1 without morpholine or "Lorol" mercaptan being present. A similar run was also made using 0.4% of morpholine. After 12 hours at 24°C. a conversion of 12% of the theoretical was obtained when neither mercaptan nor morpholine was present. The run containing 0.4% of morpholine but no mercaptan was 70.5% converted in the same time. This run shows that unlike the alkali cyanides, amines are excellent promoters in the absence of mercaptan modifiers.

#### EXAMPLE 9.

35 A run was made in accordance with the recipe given in Example 1 using 0.4% of morpholine and further modified in that 0.5% of diisopropyl xanthogen disulfide was substituted for the 0.5% of "Lorol" mercaptan. Conversion was 68% after 14½ hours at 24°C. as compared to less than 40% when the diisopropyl xanthogen disulfide was used without the morpholine promoter.

#### EXAMPLE 10.

45 A number of runs were made to determine the effect of several different amines upon the copolymerization of butadiene and acrylonitrile. The recipe was the same as in Example 1 except that the amines listed in the Table VI were used instead of morpholine. The results obtained are summarized in the following table:—

TABLE VI.  
PROMOTERS IN THE SYNTHESIS OF BUTADIENE-ACRYLONITRILE COPOLYMERS

Concentration % on Monomers	Percentage Conversion	Time Hours	Temp. °C.
Diethylaminoethanol - - - -	0	14½	24.5-26
Diethylamine - - - - -	56.5	"	24.5-26
Ethylamine - - - - -	64	"	24.5-26
Diethylamine - - - - -	64	"	24.5-26
Triethylamine - - - - -	64	"	24.5-26
N-propylamine - - - - -	64	"	24.5-26
Di-iso-propylamine - - - -	64	"	24.5-26
Butylamine - - - - -	56.5	"	24.5-26
Dibutylamine - - - - -	56.5	"	24.5-26
Tributylamine - - - - -	56.5	"	24.5-26
n-octylamine - - - - -	56.5	"	24.5-26
Lauryl amine - - - - -	54	14½	25-28
* Molecular equivalent to piperidine at concentration indicated	63	14½	25-28

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It may readily be seen from this table that diethylaminoethanol ethylamine, diethyl amine, triethyl amine, *n*-propyl amine and *n*-butyl amine gave good promoting effects. The higher alkyl amines such as dibutyl amine, tributyl amine, *n*-octylamine and lauryl amine gave no promoting effect and in some cases acted as definite poisons to the reaction.

The amine promoters of the present invention are also valuable when preparing resins such as polyacrylonitrile, polyacrylates, polymethacrylates, polyvinyl ketones or polyvinyl ethers from monolefinic materials containing a highly polar group such as a -CN, -CO- or -COOR group wherein R is a lower alkyl group such as methyl, ethyl or propyl. This is clearly demonstrated by the following example.

#### EXAMPLE 11.

Polymerization was carried out using the recipe of Example 1 but using 100 parts of acrylonitrile alone as the reactant. A yield of 27.5% of polyacrylonitrile was obtained after 16 hours at 21°C. When 0.1% of morpholine was included in the recipe, the conversion was 85% and with 0.4% of morpholine the conversion was 98% after 16 hours at 21°C.

The "Lorol" mercaptan referred to is a mixture of lauryl mercaptan with myristyl mercaptan, small amounts of other C—C aliphatic mercaptans being present, and the lauryl mercaptan predominating. It is obtained from a mixture of alcohols derived from coconut oil by hydrogenation.

The term " $C_{12}$ — $C_{14}$  mercaptan" means "Lorol" mercaptan, or lauryl mercaptans or myristyl mercaptan, as such or in admixture with each other.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the polymerization of olefinic materials in aqueous emulsion of the type referred to, wherein there is present in the reaction mixture an amount

not substantially in excess of 0.5% by weight on the reactants of a  $C_2$  to  $C_4$  amine having only one nitrogen atom per molecule.

2. A process according to Claim 1, wherein the amount of amine is from 0.05 to 0.5% by weight of the reactants.

3. A process according to Claim 1 or Claim 2, wherein the amine has an ionisation constant ranging from that of morpholine to that of piperidine.

4. A process according to any of the preceding claims, wherein the olefinic materials to be polymerized comprise diolefins with or without admixed monolefinic compounds.

5. A process according to Claim 3, wherein the amine is morpholine or piperidine.

6. A process according to Claim 4, wherein the diolefin is butadiene, isoprene, piperylene or chloroprene, and the monolefinic compound is acrylonitrile, methacrylonitrile, methyl acrylate or methyl methacrylate, an alkyl fumarate or an unsaturated ketone.

7. A process according to any of Claims 1 to 3, wherein the material to be polymerized comprises a monolefinic compound such as acrylonitrile or methacrylonitrile, an acrylic acid ester, a fumaric acid ester or an unsaturated ketone.

8. A process according to any of the preceding claims, wherein the polymerization temperature is from 20—60°C., preferably from 25—40°C.

9. A process according to any of the preceding claims, wherein there is also present in the reaction mixture, a minor proportion, of the order of 1% by weight based on the reactants, of a  $C_6$  or higher aliphatic mercaptan, preferably a  $C_{12}$ — $C_{14}$  mercaptan as hereinbefore defined.

10. A process according to any of the preceding claims, wherein the emulsifying agent and catalyst employed in the polymerization, are as hereinbefore specified.

Dated this 20th day of June, 1945.

D. YOUNG & CO.;  
29, Southampton Buildings,  
Chancery Lane, London, W.C.2,  
Agents for the Applicant.